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Pesticide residues in ginned cotton and gin motes. Case study of Zimbabwe

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ABSTRACT

Pesticides that are applied by farmers on cotton can find their way to further processes such as ginning. The contamination of cotton lint and cotton waste (such as gin motes) from the ginning process with pesticides leads to a compromise in the cotton lint quality for lint intended to be sold to the export market and may also be a source of health risk due to exposure to pesticide residues. This study therefore set forth to determine the levels of endosulfan, carbaryl, dimethoate, lambda cyhalothrin and fenvalerate in ginned cotton and gin motes. Samples were obtained from two local ginneries and soxhlet extraction was used for isolation of the pesticide residues followed by sample clean-up using solid phase extraction (SPE). The analytical procedure was done using gas chromatography with electron capture detector (GC/ECD) for endosulfan and liquid chromatography tandem mass spectrometry (LC/MS/MS) for carbaryl, dimethoate, fenvalerate and lambda cyhalothrin. Results indicated that concentrations of carbaryl and dimethoate in all samples were below detection limits. In ginned cotton maximum concentrations of endosulfan, fenvalerate and lambda cyhalothrin were 0.93ppm, 0.37ppm and 0.06ppm respectively and for gin motes 0.33ppm, 0.33ppm and 0.09ppm respectively. The presence of pesticide residues in ginned cotton and gin motes was attributed to intensive application of pesticides during cotton farming and use of persistent pesticides such as endosulfan at later stages of the plant growth.

Key words: cotton, lint, ginning, gin motes, pesticide, residue

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1. INTRODUCTION

A century of cotton production has birthed numerous industries in Zimbabwe, mainly ginning, oil pressing, textile and clothing [Esterhuizen et. al. 2015]. The bulk of cotton growing is done through contract farming under funding arrangements devised by the cotton ginning companies and contractors. Contractors normally distribute seed packs to farmers; in the process, they tend to omit the provision of other important inputs that afterwards adversely affect the production process. The inputs that the farmers acquire on their own include fertilisers and insecticides, which farmers in remote cotton-growing areas purchase through middlemen at very exploitative prices and this also leaves room for farmers to purchase toxic chemicals for pest control.

The farming of cotton in Zimbabwe involves intensive application of poisonous pesticides as chemical control is the major method used for pest management. Zimbabwe cotton lint used to command a premium in the world on account of being handpicked, clean and long staple fibre quality cotton [COMESA 2014]. The comparative advantage stemming from the aforementioned causes no longer applies, largely because of the creeping in of negative perceptions about contamination. Research points out that residues of pesticides applied on the cotton plant during growth are present in cotton lint and waste; and these are harmful to humans and the environment [Obendorf and Solbrig 1987],[Schantz et. al. 2004]. Cotton is well known as the world's "dirtiest" crop as it uses about 16% of the world's insecticides, more than any other major crop (Organic Trade Association, 2011; [Hassan 2012 and UNEP 2011]. Inhalation of cotton dust that contains pesticide residues creates increased harm to all workers who may come into contact with it during the handling and processing of the cotton lint and gin motes [NIOSH 1988].

Ginning is a mechanical process that involves the separation of cotton fibres from the seeds to give cotton lint. Ginning can be considered as an intensive blending process as fibres from different areas are blended during this process so as to improve uniformity in fibre quality. A cotton ginning facility is generally a processing plant composed of various machines, each with a specific function, arranged in sequence to unload raw seed cotton, condition it, separate the fibre (referred to as "lint") from the seed, clean the lint, dispose of the seed and trash, and bale/package the lint. Ginning is accomplished by one of two methods namely saw gins and roller gins. Cotton varieties with shorter and medium staple are ginned using a saw gin while longer fibres are ginned using a roller gin. The ginning equipment mainly used in Zimbabwe is the saw gin because the country produces medium and short staple cotton fibres. The contamination of ginned cotton and gin motes with pesticides may lead to a compromise in the export price as the local cotton may be perceived to be highly contaminated. This is highlighted by the Cotton-to-Clothing Strategy (2014-2019), which points out that the Asian market, which is one of the major export markets for local cotton and its by-products, is very particular about lint that is contamination-free.

Research points out that pesticide residues, namely synthetic pyrethroid and organophosphate residues were detected in cotton gin trash which was intended for use as stock feed [Crossan 2008]. The presence of pesticide residues in cotton dust is therefore a serious cause for concern as this dust may be released to the surrounding environment of workers processing cotton lint and gin motes. Exposure to cotton dust alone is known to cause permanent and disabled breathing difficulties that include chronic bronchitis and emphysema hence cotton dust coupled with pesticide residues may lead to more adverse health effects [NIOSH 1988]. Long term exposure to pesticide residues may lead to chronic health illnesses such as respiratory problems, memory disorders, dermatological conditions, cancer, depression, neurologic deficits, diminished intelligence, miscarriages and birth defects [McCauley et. al. 2006] [Thundiyil et. al. 2008].

1.1 MATERIALS AND METHODS

Ginned cotton and gin motes samples were obtained from two local ginning companies, in Gokwe and Sanyati. The gin batches were selected using simple random sampling and in accordance with ISO 1130-1975- sampling methods for cotton fibres. All the reagents were of analytical reagent grade and used without further purification. The pesticides carbaryl, dimethoate, endosulfan, fenvalerate and lambda cyhalothrin were pure standards of ≥98% purity purchased from Sigma Aldrich Chemical Company, Germany. All solvents and other chemicals used were of analytical grade. Anhydrous and granular sodium sulphate was used as a dehydration agent in all the extraction procedures.

1.2 Sample preparation

The cotton samples were first air-dried and cleaned up from the seeds, the seed coats and other foreign contaminants and blended using a homogeniser to ensure uniformity during the extraction process.

1.3 Extraction

Five grammes of cotton lint and gin motes samples were transferred into a sintered glass thimble. The soxhlet thimble was placed into the extraction apparatus which contained 150ml of solvent and the extraction procedure was done for 6hours. The extraction solvents used were n-hexane and acetonitrile. Sodium sulphate was used for the removal of water.

1.4 Concentration

After the extraction was complete the samples were filtered then the solution was evaporated to dryness and reconstituted in 2ml of the respective solvents.

1.5 Clean-up

Solid phase extraction was used for the clean-up step. A clean-up column was prepared with 10g of activated fluorisil in acetonitrile. Approximately 0.5g of sodium sulphate was used to top-up the column. The samples were loaded into the column, eluted with 50ml acetonitrile and collected in a 250ml flat bottomed flask. The cleaned up samples were then evaporated to dryness and further reconstituted in 1ml acetonitrile and injected on LC/MS/MS for the analysis of carbaryl, dimethoate, fenvalerate and λ-cyhalothrin. For the analysis of endosulfan on GC-ECD, the cleaned up extracts were reconstituted in 1ml n-hexane.

1.6 Analysis

Agilent 1260 LC system coupled with QTRAP® 5500 LC/MS/MS system was used for the analysis of dimethoate, carbaryl, fenvalerate and lambda cyhalothrin. The samples were separated by a Phenomenex Synergi 2.5 µm Fusion-RP 100 Å, 50 x 2.0 mm column and the guard column was a Phenomenex SecurityGuard Guard Cartridge Kit with Fusion-RP 4 x 2.0 mm cartridge. A gradient profile was followed for the LC analysis with the mobile phase constituting of water/methanol and ammonium formate buffer as follows:

Table 1. GRADIENT PROFILE

Total Time (min)	Flow Rate (µL/min)	A (%)	B (%)
0.00	400	95	5
1.00	400	95	5
6.00	400	5	95
11.00	400	5	95
11.05	400	95	5
12.00	400	95	5

A:Water/Methanol(90:10)+5mM ammonium formate

B:Methanol/Water(90:10)+5mM ammonium formate

Electrospray ionization was used for the MS/MS with positive polarity. Perkin Elmer Clarus 500, with an auto sampler was used for the analysis of alpha endosulfan, beta endosulfan and endosulfan sulphate. Duplicate analysis was done for each of the analysis and the average quantities were determined. Injection mode was set to split less with a sample injection volume of 1µL. Inlet temperature was set at 260^{0}C while µECD detector temperature was set at 300^{0}C. Ultra High Purity Nitrogen was used as the carrier gas at a constant pressure of 10psi and flow rate of 1ml/min. Chromatography column used was Equity 1701 and the temperature gradientwas as follows:

Initial: 60^{0}C (1min)

Ramp 1: 30^{0}C/min to 180^{0}C

Ramp 2: 5^{0}C/min to 250^{0}C (5min)

Ramp 3: 3^{0}C/min to 280^{0}C (10min)

3. RESULTS AND DISCUSSION

The results for the concentrations of pesticide residues in ginned cotton and gin motes for the two ginneries that were under study are shown in Figure 1. Results indicate that fenvalerate, λ-cyhalothrin and endosulfan were present in the ginned cotton samples from both ginneries whereas carbaryl and dimethoate were below the detection limits. Maximum concentrations of endosulfan in ginned cotton and gin motes were recorded as 0.93ppm and 0.33ppm respectively; for fenvalerate 0.37ppm and 0.33ppm respectively while for λ-cyhalothrin maximum concentrations were 0.06ppm and 0.09ppm respectively. Carbaryl and dimethoate were below detection limits (<0.006ppm) in all ginned cotton and gin motes samples

The presence of pesticide residues in cotton lint was mostly attributed to the persistence of the chemicals used such as endosulfan compounded by the continuous use of insecticides as farmers continue picking and spraying simultaneously as per their convenience. The detection of pesticide residues in cotton lint can also be attributed to the direct application of pesticide sprays on the opened/half opened bolls. Farmers continue to spray opened/half opened cotton bolls in an effort to curb losses that could result from attack by cotton pests such as bollworms and cotton stainers. Because of the larger surface area, most of the insecticides falling on the opened bolls get concentrated on the cotton lint and bind to the cellulose.

Endosulfan exceeded the Maximum Residue Limit (MRL) and this may be due to the persistent nature of this chemical which may still be present in further textile processes like spinning and weaving/knitting. This is because endosulfan is an organochlorine pesticide which is classified as a Persistent Organic Pollutant (POP). POPs are well known for their

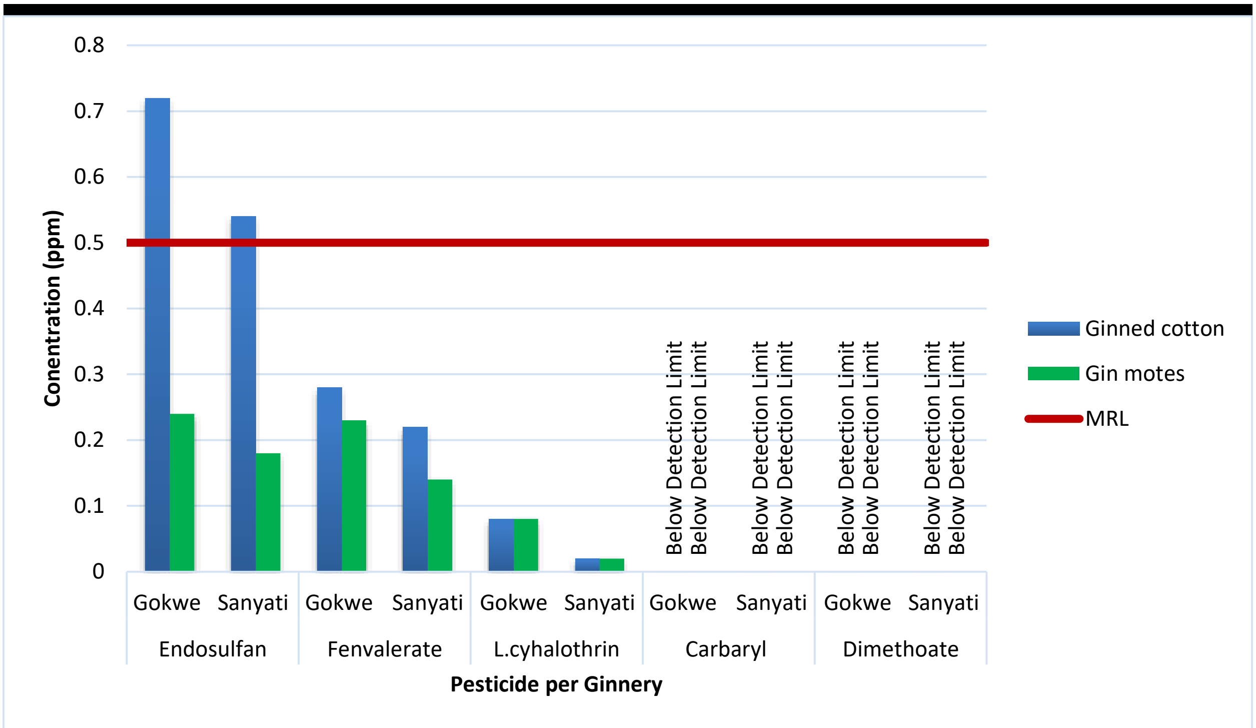

Figure 1 Pesticide residue concentrations in ginned cotton and gin motes

environmental persistence, ability to enter the human food chain, bio-accumulation and mammalian toxicity due to endocrine disruption. The other pesticides under study, that is, carbaryl, dimethoate, λ cyhalothrin and fenvalerate had quantities below the maximum recommended limits.

This indicates that these four chemicals may have degraded by the ginning period due to their less persistent nature when compared to endosulfan. The harm that is caused by these pesticides collectively may be greater than the harm they would cause individually. The use of synthetic pyrethroids with shorter half-lives such as λ-cyhalothrin should be adopted during the final growth stage of the cotton plant so as to minimize the quantity of pesticide residues. After the ginning process, the cotton lint is sold to local spinning companies, bleaching companies for making cotton wool and the rest is exported [COMESA 2013]. The presence of pesticide residues in ginned cotton, even small quantities may therefore be a cause for concern as this leads to increased contamination levels in ginned cotton which is to be sold to both local and export markets [Saungweme 2015]. Currently, Zimbabwe's major export markets are Southern African countries such as South Africa, Mozambique, Malawi and Swaziland. The country is struggling to penetrate into European and Asian markets such as China due to the perception that the local cotton lint is contaminated [Dube et. al. 2013]. Since ginning is a mechanical process which releases cotton dust into the atmosphere, lack of enforcement in health and safety issues in the local ginning companies, is of great importance as occupational exposure limits for cotton are generally not taken into serious consideration. Inhalation of cotton dust that contains pesticide residues creates increased harm to gin workers during the handling of cotton for grading and ginning processes [Berry 2007], [Revoir 1974] and [Wesley and Wall 1978]. Inhalation of cotton dust containing pesticide residues, even at low levels below the MRLs, may still be a cause for concern in addition to causing lung diseases such as bronchitis, bysinossis (occupational asthma) and lung airway obstruction which may lead to disability and premature death [NIOSH 1988, Domelsmith and Berni 1986]. According to [NIOSH 1988] a direct relationship was observed between the total concentration of cotton dust exposure and the rate of development of bysinossis. [Griffin and Columbus 1982] report that the location of a gin in relation to its dust and trash collecting equipment outside the gin was of major importance in the occurrence of dust in gins, and the dust content of ambient air outside gins also had a major impact on dust levels within gins. The presence of pesticide residues in cotton dust is therefore may cause adverse health problems this dust may be released to the surrounding environment of the ginneries [Dube et. al. 2013]. Blanket manufacturing and upholstery-making involve mechanical processes that may release cotton dust into the atmosphere. The supply of gin motes that contains pesticide residues may cause health problems as upholstery makers may inhale cotton dust that contains pesticide residues such as endosulfan during the handling of cotton gin motes [Esterhuizen 2015]. It was noted during preliminary studies that some upholstery makers are small to medium enterprises where there is severe lack of enforcement in occupational health and safety issues hence occupational exposure limits for cotton dust are not taken into serious consideration. The statistical analysis results indicate that no significant ($p>0.05$) differences were found in the pesticide concentrations in ginned cotton between the two ginneries. This may be due to the similar environmental conditions during the storage of seed cotton that is awaiting ginning and similar equipment (saw gins) and practices being used by both ginneries under study. Both Gokwe and Sanyati ginneries receive seed cotton from farmers stored in jute bags and these are left outside till the ginning process commences.

4. CONCLUSION

Environmental matters will continue to have a central role in future development of international trade in textiles therefore the supply of eco-friendly textiles in particular; pesticide-free cotton fibres can be an additional competitive advantage. Literature also indicates that there is a high incidence of diarrhoea, high infant mortality rate and a high underweight prevalence for children in the Midlands region [ZIMSTATS 2011]. Intensive pesticide usage by cotton farmers in the Midlands region may be a contributing factor to these health problems. Besides health problems caused by pesticides, these chemicals also increase production costs for cotton farmers hence leading to poor profits and that has subsequently led to the reduction in cotton lint production over the past decade. [Mubvekeri et. al. 2014] states that pesticides alone can account for 70% of variable costs hence minimising pesticide use in local cotton farming will not only lead to contaminant-free cotton lint but also a reduction in overall cotton production costs. The supply of pesticide-free cotton lint can be an additional competitive advantage as environmental matters will continue to have a central role in future development of international trade in textiles and this will enable the country to penetrate into European and Asian markets that are more environment-conscious. Further research is required to investigate the concentrations of pesticide residues in subsequent textile processing such as spinning and weaving/knitting operations. Concentrations of pesticide residues in cotton seeds during the harvesting season and after the ginning process should be investigated. This will help to determine the effects on bio-accumulation of pesticide residues in livestock as cattle are allowed to feed on the immature seed cotton left in the cotton fields and cottonseeds present in gin trash are used as stock-feed.

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